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# UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 C.F.R. § 1.53(b))

Attorney Docket No. N.C. 79,834

First Inventor or Application Identifier Pique, et al.

Title DIRECT-WRITE LASER TRANSFER AND PROCESSING

Express Mail Label No. \_\_\_\_\_

**APPLICATION ELEMENTS**

See MPEP chapter 600 concerning utility patent application contents.

1.  \* Fee Transmittal Form (e.g., PTO/SB/17)  
(Submit an original and a duplicate for fee processing)
2.  Specification [Total Pages 28]  
(preferred arrangement set forth below)
  - Descriptive title of the Invention
  - Cross References to Related Applications
  - Statement Regarding Fed sponsored R & D
  - Reference to Microfiche Appendix
  - Background of the Invention
  - Brief Summary of the Invention
  - Brief Description of the Drawings (if filed)
  - Detailed Description
  - Claim(s)
  - Abstract of the Disclosure
3.  Drawing(s) (35 U.S.C. 113) [Total Sheets 1]
4. Oath or Declaration [Total Pages 29]
  - a.  Newly executed (original or copy)
  - b.  Copy from a prior application (37 C.F.R. § 1.63(d))  
(for continuation/divisional with Box 16 completed)
    - i.  DELETION OF INVENTOR(S)  
Signed statement attached deleting inventor(s) named in the prior application, see 37 C.F.R. §§ 1.63(d)(2) and 1.33(b)

\* NOTE FOR ITEMS 1 & 13: IN ORDER TO BE ENTITLED TO PAY SMALL ENTITY FEES, A SMALL ENTITY STATEMENT IS REQUIRED (37 C.F.R. § 1.27), EXCEPT IF ONE FILED IN A PRIOR APPLICATION IS RELIED UPON (37 C.F.R. § 1.28).

ADDRESS TO: Assistant Commissioner for Patents  
Box Patent Application  
Washington, DC 20231

5.  Microfiche Computer Program (Appendix)
6. Nucleotide and/or Amino Acid Sequence Submission  
(if applicable, all necessary)
  - a.  Computer Readable Copy
  - b.  Paper Copy (identical to computer copy)
  - c.  Statement verifying identity of above copies

**ACCOMPANYING APPLICATION PARTS**

7.  Assignment Papers (cover sheet & document(s))
8.  37 C.F.R. § 3.73(b) Statement  Power of (when there is an assignee)  Attorney
9.  English Translation Document (if applicable)
10.  Information Disclosure Statement (IDS)/PTO-1449  Copies of IDS Citations
11.  Preliminary Amendment
12.  Return Receipt Postcard (MPEP 503)  
(Should be specifically itemized)
13.  \* Small Entity Statement(s)  Statement filed in prior application, (PTO/SB/09-12)  Status still proper and desired
14.  Certified Copy of Priority Document(s)  
(if foreign priority is claimed)
15.  Other: Notice of Delayed Filing of a Declaration

16. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in a preliminary amendment:

 Continuation  Divisional  Continuation-in-part (CIP) of prior application No. \_\_\_\_\_

Prior application information. Examiner \_\_\_\_\_ Group / Art Unit: \_\_\_\_\_

For CONTINUATION or DIVISIONAL APPS only: The entire disclosure of the prior application, from which an oath or declaration is supplied under Box 4b, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.

**17. CORRESPONDENCE ADDRESS**

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JC564 U.S. PTO  
09/19/00

07/19/00

PATENT APPLICATION  
Navy Case No. 79,834

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

## APPLICATION FOR LETTERS PATENT

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN THAT Alberto Pique, Douglas Chrisey, Raymond Auyeung, Huey-daw Wu, James Fitzgerald, Paul H. Kydd, and David L. Richard, who are citizens of the United States of America, and are residents of, Bowie, MD, Bowie MD, Alexandria, VA, Fairfax, VA, Laurel, MD, Lawrenceville, NJ, and Fanwood, NJ, respectively, have invented certain new and useful improvements in "DIRECT-WRITE LASER TRANSFER AND PROCESSING" of which the following is a specification:

Please Contact Preparer:  
Amy Loch Ressing  
Reg. No. 45,814  
Tel: 202-404-1558  
Date: July 11, 2000

1

2

3                   **DIRECT-WRITE LASER TRANSFER AND PROCESSING**4     This application claims the benefit of U.S. Provisional Application No. 60/144,662, filed July  
5     19, 1999.6                   **Background of the Invention**7     **1. Field of the Invention**

8         The invention relates generally to the deposition of materials and more specifically, to  
9         devices, materials and methods for direct writing of a source material onto a substrate using a  
10        first laser and then transforming the source material into a material of interest by means of a  
11        second laser.

12     **2. Description of the Related Art**

13         The term "direct write" refers generally to any technique for creating a pattern directly on  
14         a substrate, either by adding or removing material from the substrate, without the use of a mask  
15         or preexisting form. Direct write technologies have been developed in response to a need in the  
16         electronics industry for a means to rapidly prototype passive circuit elements on various  
17         substrates, especially in the mesoscopic regime, that is, electronic devices that straddle the size  
18         range between conventional microelectronics (sub-micron-range) and traditional surface mount  
19         components (10+ mm-range). (Direct writing may also be accomplished in the sub-micron  
20         range using electron beams or focused ion beams, but these techniques, because of their small  
21         scale, are not appropriate for large scale rapid prototyping.) Direct writing allows for circuits to

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1 be prototyped without iterations in photolithographic mask design and allows the rapid  
2 evaluation of the performance of circuits too difficult to accurately model. Further, direct writing  
3 allows for the size of printed circuit boards and other structures to be reduced by allowing  
4 passive circuit elements to be conformably incorporated into the structure. Direct writing can be  
5 controlled with CAD/CAM programs, thereby allowing electronic circuits to be fabricated by  
6 machinery operated by unskilled personnel or allowing designers to move quickly from a design  
7 to a working prototype. Mesoscopic direct write technologies have the potential to enable new  
8 capabilities to produce next generation applications in the mesoscopic regime. Other applications  
9 of direct write technologies in microelectronic fabrication include forming ohmic contacts,  
10 forming interconnects for circuit and photolithographic mask repair, device restructuring and  
11 customization, design and fault correction.

12 Currently known direct write technologies for adding materials to a substrate include ink  
13 jet printing, Micropen<sup>®</sup>, laser chemical vapor deposition (LCVD) and laser engineered nano-  
14 shaping (LENS). Currently known direct write technologies for removing material from a  
15 substrate include laser machining, laser trimming and laser drilling.

16 The direct writing techniques of ink jet printing, screening and Micropen<sup>®</sup> are wet  
17 techniques, that is, the material to be deposited is combined with a solvent or binder and is  
18 squirted onto a substrate. The solvent or binder must later be removed by a drying or curing  
19 process, which limits the flexibility and capability of these approaches. In addition, wet  
20 techniques are inherently limited by viscoelastic properties of the fluid in which the particles are  
21 suspended or dissolved.

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1        In the direct writing technique known as "laser induced forward transfer" (LIFT), a  
2        pulsed laser beam is directed through a laser-transparent target substrate to strike a film of  
3        material coated on the opposite side of the target substrate. The laser vaporizes the film material  
4        as it absorbs the laser radiation and, due to the transfer of momentum, the material is removed  
5        from the target substrate and is redeposited on a receiving substrate that is placed in proximity to  
6        the target substrate. Laser induced forward transfer is typically used to transfer opaque thin  
7        films, typically metals, from a pre-coated laser transparent support, typically glass, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>,  
8        SrTiO<sub>3</sub>, etc., to the receiving substrate. Various methods of laser-induced forward transfer are  
9        described in, for example, the following U.S. patents and publications incorporated herein by  
10      reference: U.S. Patent No. 4,064,205 to Landsman; U.S. Patent No. 4,752,455 to Mayer; U.S.  
11      Patent No. 4,895,735 to Cook; U.S. Patent No. 5,725,706 to Thoma et al; U.S. Patent No.  
12      5,292,559 to Joyce, Jr. et al; U.S. Patent No. 5,492,861 to Opower; U.S. Patent No. 5,725,914 to  
13      Opower; U.S. Patent No. 5,736,464 to Opower; U.S. Patent No. 4,970,196 to Kim et al; U.S.  
14      Patent No. 5,173,441 to Yu et al; U.S. Patent No. 4,987,006 to Williams et al; U.S. Patent No.  
15      5,567,336 to Tatah; U.S. Patent No. 4,702,958 to Itoh et al; German Patent No. 2113336 to  
16      Thomson-CSF and Bohandy et al, "Metal Deposition from a Supported Metal Film Using an  
17      Excimer Laser, J. Appl. Phys. 60 (4) 15 August 1986, pp 1538 - 1539. Because the film material  
18      is vaporized by the action of the laser, laser induced forward transfer is inherently a  
19      homogeneous, pyrolytic technique and typically cannot be used to deposit complex crystalline,  
20      multi-component materials or materials that have a crystallization temperature well above room  
21      temperature because the resulting deposited material will be a weakly adherent amorphous

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coating. Moreover, because the material to be transferred is vaporized, it becomes more reactive and can more easily become degraded, oxidized or contaminated. The method is not well suited for the transfer of organic materials, since many organic materials are fragile and thermally labile and can be irreversibly damaged during deposition. Moreover, functional groups on an organic polymer can be irreversibly damaged by direct exposure to laser energy. Other disadvantages of the laser induced forward transfer technique include poor uniformity, morphology, adhesion, and resolution. Further, because of the high temperatures involved in the process, there is a danger of ablation or sputtering of the support, which can cause the incorporation of impurities in the material that is deposited on the receiving substrate. Another disadvantage of laser induced forward transfer is that it typically requires that the coating of the material to be transferred be a thin coating, generally less than 1  $\mu\text{m}$  thick. Because of this requirement, it is very time-consuming to transfer more than very small amounts of material.

In a simple variation of the laser induced forward deposition technique, the target substrate is coated with several layers of materials. The outermost layer, that is, the layer closest to the receiving substrate, consists of the material to be deposited and the innermost layer consists of a material that absorbs laser energy and becomes vaporized, causing the outermost layer to be propelled against the receiving substrate. Variations of this technique are described in, for example, the following U.S. patents and publications incorporated herein by reference: U.S. Patent No. 5,171,650 to Ellis et al, U.S. Patent No. 5,256,506 to Ellis et al, U.S. Patent No. 4,987,006 to Williams et al, U.S. Patent No. 5,156,938 to Foley et al and Tolbert et al, "Laser Ablation Transfer Imaging Using Picosecond Optical pulses: Ultra-High Speed, Lower

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1 Threshold and High Resolution" Journal of Imaging Science and Technology, Vol. 37, No. 5,  
2 Sept./Oct. 1993pp.485-489. A disadvantage of this method is that, because of the multiple layers,  
3 it is difficult or impossible to achieve the high degree of homogeneity of deposited material on  
4 the receiving substrate required, for example, for the construction of electronic devices, sensing  
5 devices or passivation coatings.

6 The direct write technique called laser chemical vapor deposition (LCVD) utilizes a laser  
7 beam focused on the surface of a substrate to induce localized chemical reactions. Usually the  
8 surface of the substrate is coated with a metal-organic precursor, which is either pyrolyzed or  
9 photolyzed locally where the laser beam scans. Pyrolytic laser CVD involves essentially the  
10 same mechanism and chemistry as conventional thermal CVD, and it has found major use in  
11 direct writing of thin films for semiconductor applications. In photolytic CVD, the chemical  
12 reaction is induced by the interaction between the laser light and the precursors. A limitation of  
13 both processes is that they must be carried out under controlled atmospheres such as inside a  
14 vacuum system and they tend to exhibit slow deposition rates. In addition, they are not well  
15 suited for direct write applications where multilayers of dissimilar materials need to be  
16 produced.

17 The direct write technique called LENS, utilizes a laser beam to melt powders of various  
18 materials as they come in contact with the substrate surface. LENS is a process that works well  
19 for making thick layers of metals, however, the high melting points exhibited by most ceramics  
20 required the use of high power laser beams that cause overheating of the substrate and  
21 surrounding layers. Furthermore, many ceramics once melted will not exhibit their original

Inventor's Name: Alberto Piqué, Raymond C.Y. Auyeung, James Fitzgerald, Douglas B. Chrisey, Huey-Daw Wu, Paul Kydd and David L. Richard

1 crystalline structure after solidification. In addition, because the materials being deposited must  
2 first melt and then resolidify, the layers are under large stresses which can cause their  
3 delamination.

4 A direct write method of laser transfer of certain types of materials is described in U.S.  
5 Patent Application No. 09/318,134 for "MATRIX ASSISTED PULSED LASER  
6 EVAPORATION DIRECT WRITE" filed on May 25, 1999 by Chrisey et al.

7 There are some materials that are easier to transfer in a precursor state or as a mixture of  
8 a precursor and a powdered form, but when they are transferred in this form, they do not have  
9 desired physical properties such as electrical conductance. In order to optimize desired qualities  
10 such as electrical conductance, further processing of the materials is necessary. Therefore, there  
11 is a strong need for devices and methods for transferring materials in a precursor form under  
12 ambient conditions (that is, atmospheric pressure and room temperature), and then transforming  
13 the precursor into a more useful or desirable form.

15 **Summary of the Invention**

16 It is an object of the present invention to provide devices, materials and methods for  
17 creating a deposit of a material of interest on a substrate wherein a precursor to the material is  
18 deposited which can immediately be transformed into the material of interest.

19 It is an object of the present invention to provide a device and method for creating  
20 deposits of metals, dielectrics, ferroelectrics, ferrites and phosphors.

21 It is an object of the present invention to provide a device and method that is useful for

Inventor's Name: Alberto Piqué, Raymond C.Y. Auyeung, James Fitzgerald, Douglas B. Chrisey, Huey-Daw Wu, Paul Kydd and David L. Richard

1 creating a deposit of electrically conducting material by depositing a precursor material or a  
2 mixture of a precursor material and an inorganic powder that is transformed into an electrical  
3 conductor.

4 It is an object of the present invention to provide a device and method that allows for  
5 laser transfer and laser processing of a material to occur in sequential steps.

6 These and other objects are achieved by a device and method for creating a deposit of a  
7 material of interest on a receiving substrate, the device comprising a first laser and second laser,  
8 a receiving substrate, and a target substrate. The target substrate comprises a laser transparent  
9 support that has a source material coated on a front surface. The first laser can be positioned so  
10 that a laser beam from the first laser can be directed through the back surface of the target  
11 substrate and through the laser-transparent support to strike the coating at a defined location with  
12 sufficient energy to remove or lift the source material from the surface of the support. The  
13 receiving substrate can be positioned in a spaced relation to the target substrate so that the source  
14 material is deposited at a defined location on the receiving substrate. The second laser is then  
15 positioned to strike the deposited source material to transform the source material into the  
16 material of interest.

17 **Brief Description of the Drawings**

18 A more complete appreciation of the invention will be readily obtained by reference to  
19 the following Description of the preferred Embodiments and the accompanying drawings.

20 Figure 1a is a schematic representation of the apparatus of the present invention during  
21 the operation of the first laser.

1           Figure 1b is a schematic representation of the apparatus of the present invention during  
2       the operation of the second laser.

3       **Detailed Description of the Preferred Embodiments**

4           As schematically illustrated in Figure 1a and 1b, the apparatus of the present invention  
5       includes a first laser 12, a second laser 112, a target substrate having a laser transparent support  
6       15 and a coating 16, and a receiving substrate 18. As shown schematically in Figure 1a, the first  
7       laser is positioned so that as it emits a laser beam 14, the beam takes an optical path so that it  
8       travels through the back surface of the target substrate and through the laser transparent support  
9       15 to strike the coating 16, which comprises a source material. The receiving substrate 18 is  
10      positioned so that when the source material is removed from the target substrate by the action of  
11      the laser beam, the source material is deposited on the receiving substrate. As shown  
12      schematically in Figure 1b, the second laser is positioned so that as it emits a laser beam 114, the  
13      beam takes an optical path so that it travels through the laser transparent support and strikes a  
14      deposit 116 of the source material on the substrate. The first laser, the second laser, the target  
15      substrate and the receiving substrate are connected to first laser positioning means 20, second  
16      laser positioning means 120, target substrate positioning means 22 and receiving substrate  
17      positioning means 24, respectively. As discussed below, the apparatus may also include first  
18      laser shuttering means 30 and second laser shuttering means 130, reflective means 40 and 140  
19      and an objective 50.

20           Preferably, the first laser and the second laser are copropagating or coaxial, that is, they  
21       use substantially the same optical pathway. Preferably, the apparatus includes shuttering means,

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1 such as an electro-mechanical, electro-optical or electro-acoustic shuttering device to control the  
2 timing of the two laser beams and includes reflective means, such as mirrored surfaces to direct  
3 the paths of the laser beams. An objective lens serves to focus the beams onto the target substrate  
4 or through a transparent portion of the target substrate and onto the receiving substrate.

5 However, the method of the invention could also be carried out with a second laser that does not  
6 travel through the target substrate, but rather strikes the receiving substrate directly. Further, the  
7 method of the invention could be carried out with laser pulses from a single laser source, with  
8 adjustments made in the wavelength, pulse width, relative timing, polarization and power.

9         The receiving substrate can be any material, planar or non-planar onto which one may  
10 wish to create a deposit. The receiving substrate may be any solid material including, but not  
11 limited to, silicon, glass, plastics, metals, and ceramics. The receiving substrate may be  
12 maintained at a constant temperature by heating or cooling, preferably in the range of -50 to 300  
13 °C. Cooling may be used to aid the adhesion of the source material to the receiving substrate.  
14 Heating may be used to accelerate or facilitate the conversion of the source material into the  
15 material of interest.

16         The present invention is particularly useful in creating electronic devices such as passive  
17 and active components of printed circuit boards (PCBs).

18         The term "source material" as used herein refers to any material that can be deposited on  
19 a receiving substrate and that can be processed or transformed by the action of a laser to give a  
20 material of interest. The source material may be a single compound or a mixture of different  
21 compounds and/or different phases, such as mixed liquids and powders. And, as used herein,

Inventor's Name: Alberto Piqué, Raymond C.Y. Auyeung, James Fitzgerald, Douglas B. Chrisey, Huey-Daw Wu, Paul Kydd and David L. Richard

1 what is meant by "processing" or "transforming" the source material into the material of interest  
2 is any action effected by the second laser that changes the composition or the properties of the  
3 deposited material. For example, the heating action of the second laser may cause a chemical  
4 change or decomposition of all or a portion of a source material or a change in conductivity or  
5 density in the source material. The act of transforming may also include any interaction of the  
6 source material with the substrate or with previously deposited material.

7 For creating deposits of metals, such as for conductor lines, any precursors commonly  
8 used in chemical vapor deposition(CVD) and laser-induced chemical vapor depositon (LCVD)  
9 may be used. Examples include, but are not limited to, metal alkoxides, metal diketonates and  
10 metal carboxalates.

11 The source material may also be a homogeneous mixture of a liquid organometallic and a  
12 metal powder. When this material is transferred onto the receiving substrate, the second laser  
13 acts to decompose the organometallic to form bridges connecting the grains of metal powder.  
14 Use of a liquid/powder source material allows a dramatic increase in the mass of material that  
15 can be transferred per laser shot, which results in a faster layer growth rate. The particle size of  
16 the metal powder is typically about 0.01 to about 5 microns. Specific examples of liquid  
17 organometallic/metal powder combinations include silver I 2,4-pentanedionate with silver  
18 powder, silver neodecanoate with silver powder, platinum 2,4-pentanedionate with platinum  
19 powder, indium 2,4-pentanedionate with indium powder, copper II 2,4-pentanedionate with  
20 copper powder, and indium acetylacetone with indium powder. Further examples of materials  
21 that can be used as the source material to create conducting deposits are described in the

Inventor's Name: Alberto Piqué, Raymond C.Y. Auyeung, James Fitzgerald, Douglas B. Chrisey, Huey-Daw Wu, Paul Kydd and David L. Richard

1 following patents incorporated herein by reference: U.S. Patent No. 5,358,643 to Hampden-  
2 Smith et al; U.S. Patent No. 5,278,138 to Ott et al; U.S. Patent No. 5,439,502 to Kodas et al;  
3 U.S. Patent No. 5,616,165 to Glicksman et al; U.S. Patent No. 5,656,329 to Hampden-Smith et  
4 al; U.S. Patent No. 5,882,722 to Kydd.

5 For creating deposits of ceramics, such as for dielectric layers and ferroelectric and  
6 ferrite materials and phosphors, the source material may be any material that is commonly used  
7 as a precursor in sol-gel processes. For example, to make simple oxide ceramics, the source  
8 material can be a simple hydrated alkoxide. Mixed liquid-powders can be used such as, for  
9 example, aluminum isopropoxide with  $\text{Al}_2\text{O}_3$  or alumina. To make a complex oxide, the source  
10 material can be, for example, a double metal alkoxide. Mixed liquid-powder combinations  
11 include barium titanium ethylhexano-isopropoxide with barium titanate powder and strontium  
12 titanium isopropoxide with strontium titanate powder.

13 The material of interest can be any material that one may wish to have created on a  
14 substrate in a defined pattern. Typically, the material of interest is an inorganic material (since  
15 an organic material would decompose by the action of the second laser). Examples of inorganic  
16 materials include, but are not limited to the following:

17 Metals, including, but not limited to silver, nickel, gold, copper, chromium, titanium,  
18 aluminum, platinum, palladium, etc., and alloys thereof;

19 Ceramics, including, but not limited to alumina ( $\text{Al}_2\text{O}_3$ ), silica and other glasses, and  
20 dielectrics (see below);

21 Dielectrics, including, but not limited to alumina, magnesium oxide ( $\text{MgO}$ ), yttrium

Inventor's Name: Alberto Piqué, Raymond C.Y. Auyeung, James Fitzgerald, Douglas B. Chrisey, Huey-Daw Wu, Paul Kydd and David L. Richard

- 1 oxide( $\text{Y}_2\text{O}_3$ ), zirconium oxide ( $\text{ZrO}_2$ ), cerium oxide ( $\text{CeO}_2$ ), etc.;
- 2 Ferroelectrics, including, but not limited to barium titanate ( $\text{BaTiO}_3$ ), strontium titanate  
3 ( $\text{SrTiO}_3$ ), lead titanate ( $\text{PbTiO}_3$ ), lead zirconate ( $\text{PbZrO}_3$ ), potassium niobate ( $\text{KNbO}_3$ ), strontium  
4 bismuth tantalate ( $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ), ( $\text{Ba},\text{Sr}\text{TiO}_3$ , and solid solution stoichiometric variations thereof,  
5 etc. ;
- 6 Piezoelectrics, including, but not limited to the above mentioned ferroelectrics, quartz,  
7 AlN, etc.;
- 8 Ferrites, including but not limited to yttrium iron garnet ( $\text{Y}_3\text{Fe}_5\text{O}_{12}$ ), barium zinc ferrite  
9 ( $\text{Ba}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{19}$ ), hexagonal ferrites such as barium ferrite, spinel ferrites such as nickel zinc  
10 ferrites, manganese zinc ferrite, magnetite ( $\text{Fe}_3\text{O}_4$ ), etc.;
- 11 Electro-optical ceramics, including, but not limited to lithium niobate ( $\text{LiNbO}_3$ ), lithium  
12 tantalate ( $\text{LiTaO}_3$ ), cadmium telluride ( $\text{CdTe}$ ), zinc sulfide ( $\text{ZnS}$ ), etc.;
- 13 Ceramic superconductors, including, but not limited to  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (YBCO),  
14  $\text{Tl}_2\text{CaBa}_2\text{Cu}_3\text{O}_{12}$ ,  $\text{La}_{1.4}\text{Sr}_{0.6}\text{CuO}_{3.1}$ ,  $\text{BiSrCaCuO}$ ,  $\text{BaKBiO}$ , halide doped fullerenes,etc.;
- 15 Chalcogenides, including, but not limited to  $\text{SrS}$ ,  $\text{ZnS}$ ,  $\text{CaS}$ ,  $\text{PbS}$ , etc.;
- 16 Semiconductors, including, but not limited to Si, Ge, GaAs, CdTe, etc.;
- 17 Phosphors, including, but not limited to  $\text{SrS}:\text{Eu}$ ,  $\text{SrS}:\text{Ce}$ ,  $\text{ZnS}:\text{Ag}$ ,  $\text{Y}_2\text{O}_2:\text{Eu}$ ,  $\text{Zn}_2\text{SiO}_4:\text{Mn}$ ,  
18 etc. ;
- 19 and
- 20 Transparent conductive oxides, including, but not limited to indium tin oxide, zinc oxide,  
21 etc.

Inventor's Name: Alberto Piqué, Raymond C.Y. Auyeung, James Fitzgerald, Douglas B. Chrisey, Huey-Daw Wu, Paul Kydd and David L. Richard

1           As described above, source materials for these materials of interest may be readily  
2           synthesized by, for example, providing an inorganic-organic precursor or combining an  
3           inorganic material in powdered form with an inorganic-organic precursor.

4           The source material may be applied to the front surface of the laser transparent support  
5           by any method known in the art for creating uniform coatings on a surface, including, for  
6           example, by doctor blading, roller coating, screen printing, spin coating, ink jet deposition, spin  
7           spray coating, aerosol spray deposition, electrophoretic deposition, pulsed laser deposition,  
8           matrix assisted pulsed laser evaporation, thermal evaporation, sol gel deposition, chemical vapor  
9           deposition, sedimentation and print screening. Typically, the source material will be applied to  
10          the front surface of the laser transparent substrate to form a coating that is between about 0.1  $\mu\text{m}$   
11          and about 10  $\mu\text{m}$  in thickness.

12          The laser transparent support is typically planar, having a front surface that is coated with  
13          the source material and a back surface that can be positioned so that laser energy from the first  
14          laser can be directed through the support. The composition of the laser transparent support is  
15          selected in accordance with the particular types of laser that is used. For example, if the laser is  
16          a UV laser, the laser transparent support may be a UV-transparent material including, but not  
17          limited to fused silica or sapphire. If the laser is an IR laser, the laser transparent support may be  
18          an IR-transparent material including, but not limited to plastic, silicon, fused silica, or sapphire.  
19          Similarly, if the laser is a visible laser, the laser transparent support may be a material that is  
20          transparent in the visible range, including, but not limited to soda-lime and borosilicate glasses.  
21          Typically, the method of the present invention will involve the use of both UV and IR lasers, and

Inventor's Name: Alberto Piqué, Raymond C.Y. Auyeung, James Fitzgerald, Douglas B. Chrisey, Huey-Daw Wu, Paul Kydd and David L. Richard

1 the preferred laser transparent material is a material that is transparent to both.

2 The first laser can be any type such as is generally used with laser deposition. The laser  
3 wavelength and pulse energy are chosen so that the source material on the target substrate  
4 absorbs sufficient laser energy to result in the removal of the source material from the laser  
5 transparent support and the deposit of the source material on the receiving substrate. Typically,  
6 the particular laser is selected with regard to the absorption wavelengths of the source material.

7 Lasers are commercially available within the full spectral range from UV to IR. Examples of  
8 suitable lasers include, but are not limited to, pulsed gas lasers such as excimer lasers, i.e. F<sub>2</sub>  
9 (157 nm), ArF (193 nm), KrF (248 nm). XeCl (308 nm), XeF (351 nm), CO<sub>2</sub>, nitrogen, metal  
10 vapor, etc., pulsed solid state lasers such as Nd:YAG, Ti:Sapphire, Ruby, diode pumped,  
11 semiconductor, etc., and pulsed dye laser systems. Examples of laser wavelengths employed  
12 include the UV emissions from excimer lasers operating at 193 and 248 nm and the frequency  
13 tripled or quadrupled emission from a Nd:YAG laser operating at 355 nm or 266 nm,  
14 respectively. In this fashion the chemical source material is transferred over the surface of the  
15 receiving substrate at a defined location over an area proportional to the area illuminated on the  
16 target substrate by the laser pulse and the target substrate-receiving substrate distance. The laser  
17 energy is chosen such as to be sufficient to vaporize the first monolayers of the source material  
18 at the interface without causing the rest of the material to heat up above its decomposition  
19 temperature. Typical laser fluences utilized range from 0.01 to 1 J/cm<sup>2</sup>. The second step of the  
20 process begins once the chemical source material has been transferred to the surface of the  
21 receiving substrate. A second laser pulse or beam of the same or different wavelength and with a

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1 spot size of the same or a different size as that of the first laser is fired through the transparent  
2 target substrate so it hits the source material deposited over the receiving substrate. The effect of  
3 the second laser causes the decomposition or transformation of the chemical source material into  
4 the material of interest. This second "processing" laser pulse typically requires the use of an IR  
5 laser, for example the fundamental emission from a Nd:YAG laser operating at 1064 nm with  
6 power densities of kw/cm<sup>2</sup> and with pulse lengths ranging from 10 nanoseconds to a few hundred  
7 microseconds. The second laser may also be a continuous wave laser with or without a chopper.  
8 Alternately, a longer wavelength CO<sub>2</sub> laser operating at 10.6 μm can also be used. The interval  
9 between the first transfer, and second processing laser pulses can be as short as 1 microsecond.  
10 The first laser and the second laser, as well as the target substrate and the receiving substrate can  
11 be moved independently from each other or in any type of combination in order to deposit and  
12 process the material forming any given pattern.

13 In addition, the receiving substrate can be heated or cooled and maintained at a constant  
14 temperature, preferably between -50 and 300 °C. Heating the substrate accelerates the removal  
15 of the volatile components still present in the transferred source material and improves the  
16 mechanical and electrical properties of the material of interest.

17 The first laser, the second laser, the target substrate and the receiving substrate can be  
18 positioned with respect to each other and moved with respect to each other by any means known  
19 in the art for supporting a laser, target substrate and receiving substrate and moving them in a  
20 controlled and defined manner. For example, similar positioning means and moving means for a  
21 laser, target and receiving substrate are known in the fields of laser transfer deposition and laser

Inventor's Name: Alberto Piqué, Raymond C.Y. Auyeung, James Fitzgerald, Douglas B. Chrisey, Huey-Daw Wu, Paul Kydd and David L. Richard

1 induced forward transfer. The first laser may be positioned in any location that provides an  
2 optical path between itself and the target substrate so that sufficient laser energy can be directed  
3 to defined positions on the target substrate. The dimensions of the laser beam can be controlled  
4 by any means known in the art so that only a precisely defined area of the target substrate is  
5 exposed to the laser energy and so that only a precisely defined portion of the coating is  
6 removed. The receiving substrate should be positioned so that when the coating on the target  
7 substrate is removed, the transfer material can be deposited at a defined location on the receiving  
8 substrate. Preferably, the receiving substrate is positioned about 10 to about 100  $\mu\text{m}$  from the  
9 coating on the front surface of the target substrate. The second laser may be positioned in any  
10 location that provides an optical path between itself and the receiving substrate so that only a  
11 precisely defined portion of the receiving substrate is hit by the laser beam. Typically, the second  
12 laser beam will pass through a transparent portion of the target substrate (such as an area where  
13 the coating has just been removed by the action of the first laser.) The area of the receiving  
14 substrate that is exposed to the second laser will typically be the same as the area of the deposit  
15 of source material, but it can also be made larger or smaller. For example, the area of the second  
16 laser may be adjusted so that a larger section of deposited source material resulting from  
17 successive transfers can be processed at the same time. The first laser, the second laser, target  
18 substrate, and the receiving substrate should be moveable with respect to each other so that the  
19 source material can be deposited in a pattern and then processed either immediately or  
20 subsequently. (As used herein, the terms "moving [a] with respect to [b]" or "moving [a] and [b]  
21 with respect to each other" mean that either [a] or [b] can be moved to effect a change in their

Docket No.: N.C. 79,834

PATENT APPLICATION

Inventor's Name: Alberto Piqué, Raymond C.Y. Auyeung, James Fitzgerald, Douglas B. Chrisey, Huey-Daw Wu, Paul Kydd and David L. Richard

1 relative position.)

Having described the invention, the following examples are given to illustrate specific applications of the invention, including the best mode now known to perform the invention.

4 These specific examples are not intended to limit the scope of the invention described in this  
5 application.

## EXAMPLES

### Example 1: Laser Transfer and Processing of Silver (Ag)

A conducting silver line was fabricated by using a UV laser beam to first transfer the coating from a target substrate to a receiving substrate and then post-processing the transferred material with a second IR laser beam. The target substrate consisted of a UV grade fused silica disk of 2" diameter and approx. 1/8" thickness on which one side was coated with a layer of the material to be transferred. This layer consisted of Ag powder (particle size of a few microns) and a metalloorganic precursor which decomposes into a conducting specie(s) at low temperatures (less than 200 °C). The receiving substrate was a microwave-quality circuit board which has various gold electrode pads that are a few microns thick. A spacer of 25-micron thickness was used to separate the target and receiving substrates.

Silver was first transferred with a focused UV ( $\lambda = 248$  nm or  $\lambda = 355$ ) laser beam through the target substrate at a focal fluence of  $225\text{ mJ/cm}^2$ . The spot size at the focus was  $40\text{ }\mu\text{m}$  in diameter. A line of “dots” was fabricated between 2 gold contact pads by translating both the target and receiving substrates together to expose a fresh area of the target substrate for each laser shot while the laser beam remained stationary. The distance between the laser spots was

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1 approx. one spot diameter. A pass consisted of approximately 25 dots and a total of 10 passes  
2 (superimposed on one another) was made. The target substrate was moved between each pass.  
3 After the transfers, the resistance between the gold pads as measured with an ohmmeter was  
4 infinite (> 20-30 Megaohms).

5 Next, a flashlamp-pumped Nd:YAG laser operating at 1.064  $\mu\text{m}$  at 40 Hz with no Q-  
6 switch (i.e. free-running operation) was focused onto this silver line. The pulse width of this IR  
7 laser beam was estimated to be a few hundred microseconds and the focal spot size was approx.  
8 40 microns in diameter. The average focal power density was of the order of a few kW/cm<sup>2</sup>. Six  
9 passes over the previously transferred silver line were performed with this IR beam and the  
10 measured resistance decreased after each pass. Final resistance was 10.9 ohms and the IR laser  
11 post-processing was stopped because the measured resistance began to increase. The resistance  
12 of this silver line was also measured on an impedance analyzer at 1 MHz and the calculated  
13 resistivity was approx. 100 times that of bulk silver. The color of the silver line also changed  
14 from dark (almost black) right after the UV transfer to a beige appearance after the last IR  
15 processing pass.

16 In another variation of this experiment, the UV laser beam (wavelength of 355 nm) and  
17 the IR processing laser beam ( $\lambda = 1064 \text{ nm}$ ) were both incident on the target substrate at the  
18 same time. This was an attempt to both transfer the silver material and "process" it at the same  
19 time.

20

21 **Example 2: Laser Transfer and Processing of Barium Titanate (BaTiO<sub>3</sub>)**

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1       Using a method similar to that described in example 1), the ferroelectric material BaTiO<sub>3</sub>  
2       (BTO) was transferred to interdigitated capacitor structures on an MgO substrate.

3           The receiving substrate has interdigitated capacitors of various finger lengths and gap  
4       spacings patterned on a (500 Å)Au/(1.5 µm)Ag/(500Å)Cr coating on an MgO substrate. The  
5       target substrate consisted of a mixture of BTO powders in a precursor agent comprising barium  
6       neodecanoate and dimethoxy titanium deneodecanoate deposited as a layer on one side of a UV-  
7       grade fused silica disk.

8           The UV transfer laser wavelength was 248 nm and the focal laser fluence on the target  
9       substrate was 0.3 J/cm<sup>2</sup>. The focal spot size was 40 microns in diameter. The UV laser  
10      operated at 1 Hz and the target substrate was moved after every laser shot to expose a fresh area  
11      of the BTO coating. (A 25-micron spacer was used between the target and receiving substrates).  
12      Structures such as "pads" or "dots" could be built by translating the receiving substrate. Areas  
13      of the substrate which received little or no material were "repaired" subsequently by repeated  
14      transfers over the same site.

15           A BTO pad was built over the fingers of the interdigitated capacitors by UV laser  
16       transfer and then a portion of it processed by an IR laser (=1064 nm). The estimated IR laser  
17       focal spot was approx. 42 microns in diameter yielding an average intensity in the kW/cm<sup>2</sup>  
18       range. The IR laser beam was allowed to remain stationary over a portion of the BTO pad for 24  
19       sec.

20           Under optical microscopy, the "laser processed" portion of the BTO pad appeared more  
21       shiny and glassy than the original BTO transfer. The interdigitated capacitors were measured on

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- 1       an impedance analyzer near 30 GHz and the dielectric constant was approximately 30.
- 2              Obviously, many modifications and variations of the present invention are possible in
- 3              light of the above teachings. It is therefore to be understood that, within the scope of the
- 4              appended claims, the invention may be practiced otherwise than as specifically described.

Claims

What is claimed is:

1. An apparatus for creating a deposit of a material of interest on a substrate, the apparatus comprising

a first laser, wherein the first laser is a pulsed laser,

a second laser,

a receiving substrate, and

a target substrate comprising a laser-transparent support having a back surface and a front surface, wherein the front surface has a coating that comprises a source material, wherein the source material is a material that can be transformed into the material of interest,

means for positioning the first laser in relation to the target substrate so that pulsed laser energy can be directed through the back surface of the target substrate and through the laser-transparent support to strike the coating at a defined target location with sufficient energy to cause the source material to be removed from the surface of the support at the defined target location,

means for positioning the receiving substrate in a spaced relation to the target substrate so that the source material can migrate from the space between the receiving substrate and the target substrate and can be deposited at a defined receiving location on the receiving substrate,

and

means for positioning the second laser so that laser energy can strike the source material that is deposited on the receiving substrate with sufficient energy to transform the source material into the material of interest.

2. The apparatus of Claim 1 wherein the first laser and the second laser are copropagating and coaxial.

3. The apparatus of Claim 2 further including shuttering means wherein the first laser or the second laser can be selected.

4. The apparatus of Claim 1 wherein the source material is a homogeneous mixture of an organometallic compound and a metal powder.

5. The apparatus of Claim 1 wherein the source material is a organometallic/metal powder combination selected from the group consisting of

silver I 2,4-pentanedionate/silver;

silver neodecanoate/silver;

platinum 2,4-pentanedionate/platinum;

indium 2,4-pentanedionate/indium;

copper II 2,4-pentanedionate/copper; and

indium acetylacetonate/indium.

6. The apparatus of Claim 1 wherein the source material is a homogeneous mixture of a hydrated metal alkoxide and a metal powder.

7. The apparatus of Claim 1 wherein the source material is a homogeneous mixture of an organometallic compound and an inorganic oxide powder.

8. The apparatus of Claim 1 wherein the source material is a mixture of a hydrated inorganic alkoxide and an inorganic oxide powder.

9. The apparatus of Claim 1 wherein the source material is a mixture of aluminum isopropoxide and aluminum oxide powder.

10. The apparatus of Claim 1 wherein the source material is an inorganic alkoxide/inorganic oxide mixture selected from the group consisting of barium titanium ethylhexano-isopropoxide/barium titanate powder and strontium titanium isopropoxide/strontium titanate powder.

11. The apparatus of Claim 1 wherein the source material is a mixture of one or more metal

organic compounds.

12. The apparatus of Claim 1 wherein the source material is a mixture of one or more hydrated metal alkoxides.

13. The apparatus of Claim 1 wherein the first laser is a pulsed UV laser and the second laser is an IR laser.

14. The apparatus of Claim 1 further including means to maintain the receiving substrate at a constant temperature between -50 and 300 °C.

15. A method for creating a deposit of a material of interest on a receiving substrate, the method comprising the steps of

providing a first laser and a second laser, wherein the first laser is a pulsed laser,

providing a receiving substrate,

providing a target substrate comprising a laser-transparent support having a back surface and a front surface, wherein the front surface has a coating that comprises a source material,

wherein the source material is a material that can be transformed into the material of interest,

positioning the first laser in relation to the target substrate and exposing the target

substrate to pulsed laser energy so that the pulsed laser energy is directed through the back

surface of the target substrate and through the laser-transparent support to strike the coating at a defined target location with sufficient energy to cause the source material to be removed from the surface of the support at the defined location,

positioning the receiving substrate in a spaced relation to the target substrate so that the source material is deposited at defined receiving location on the receiving substrate, and

positioning the second laser in relation to the receiving substrate so that laser energy strikes the deposited source material to transform the source material into the material of interest.

16. The method of Claim 15 including the further step of pretreating the receiving substrate by positioning the first laser or the second laser so that it strikes the receiving substrate before the source material is deposited thereon.

17. The method of Claim 15 wherein the receiving substrate is maintained at a constant temperature of between -50 °C and 300 °C.

18. The method of Claim 15 wherein the source material is a homogeneous mixture of an organometallic compound and a metal powder.

19. The method of Claim 15 wherein the source material is a organometallic/metal powder

combination selected from the group consisting of

silver I 2,4-pentanedionate/silver;  
silver neodecanoate/silver;  
platinum 2,4-pentanedionate/platinum;  
indium 2,4-pentanedionate/indium;  
copper II 2,4-pentanedionate/copper; and  
indium acetylacetonate/indium.

20. The method of Claim 15 wherein the source material is a homogeneous mixture of a hydrated metal alkoxide and a metal powder.
21. The method of Claim 15 wherein the source material is a hydrated metal alkoxide.
22. The method of Claim 15 wherein the source material is a mixture of aluminum isopropoxide and aluminum oxide powder.
23. The method of Claim 15 wherein the source material is an inorganic alkoxide/inorganic oxide mixture selected from the group consisting of barium titanium ethylhexano-isopropoxide/barium titanate powder and strontium titanium isopropoxide/strontium titanate powder.

24. The method of Claim 15 wherein the source material is a mixture of one or more metal organic compounds.

25. The method of Claim 15 wherein the source material is a mixture of one or more hydrated metal alkoxides.

26. A method for creating a deposit of a material of interest on a receiving substrate, the method comprising the steps of

providing a target substrate comprising a laser-transparent support having a back surface and a front surface, wherein the front surface has a coating that comprises a source material, wherein the source material is a material that can be transformed into the material of interest,

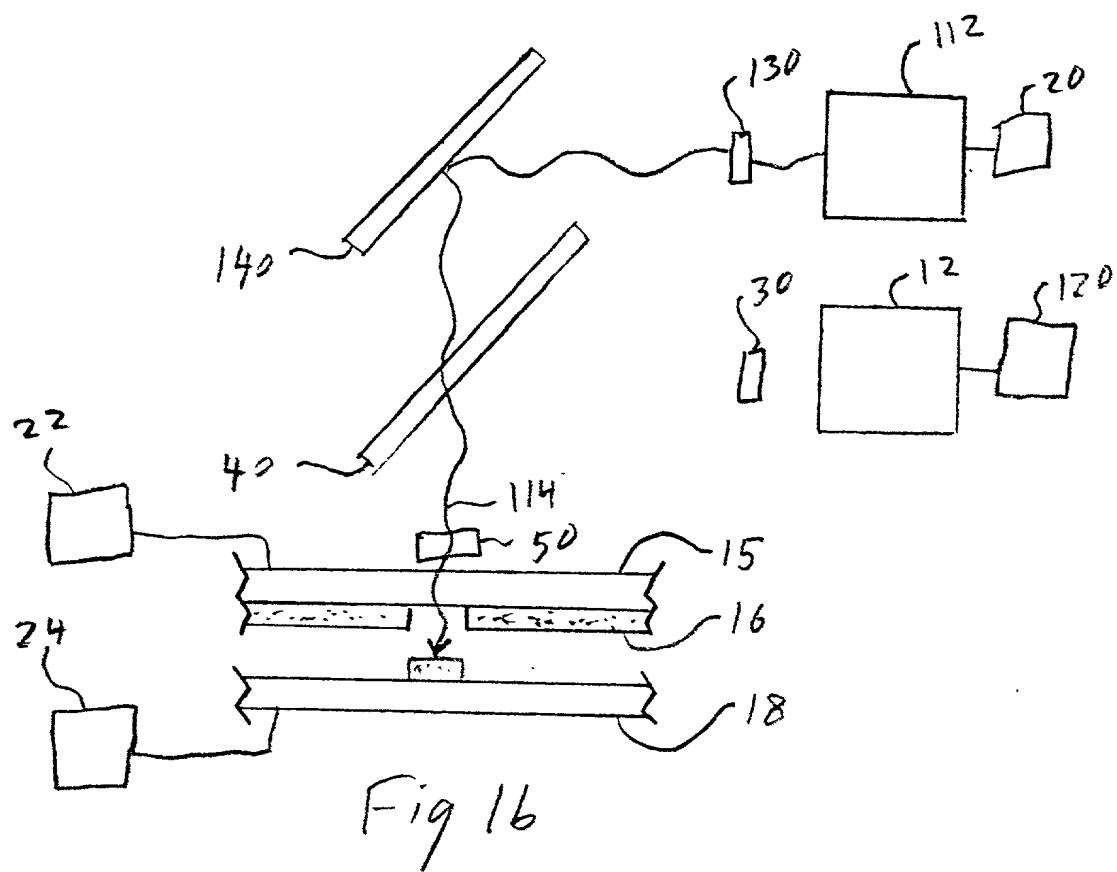
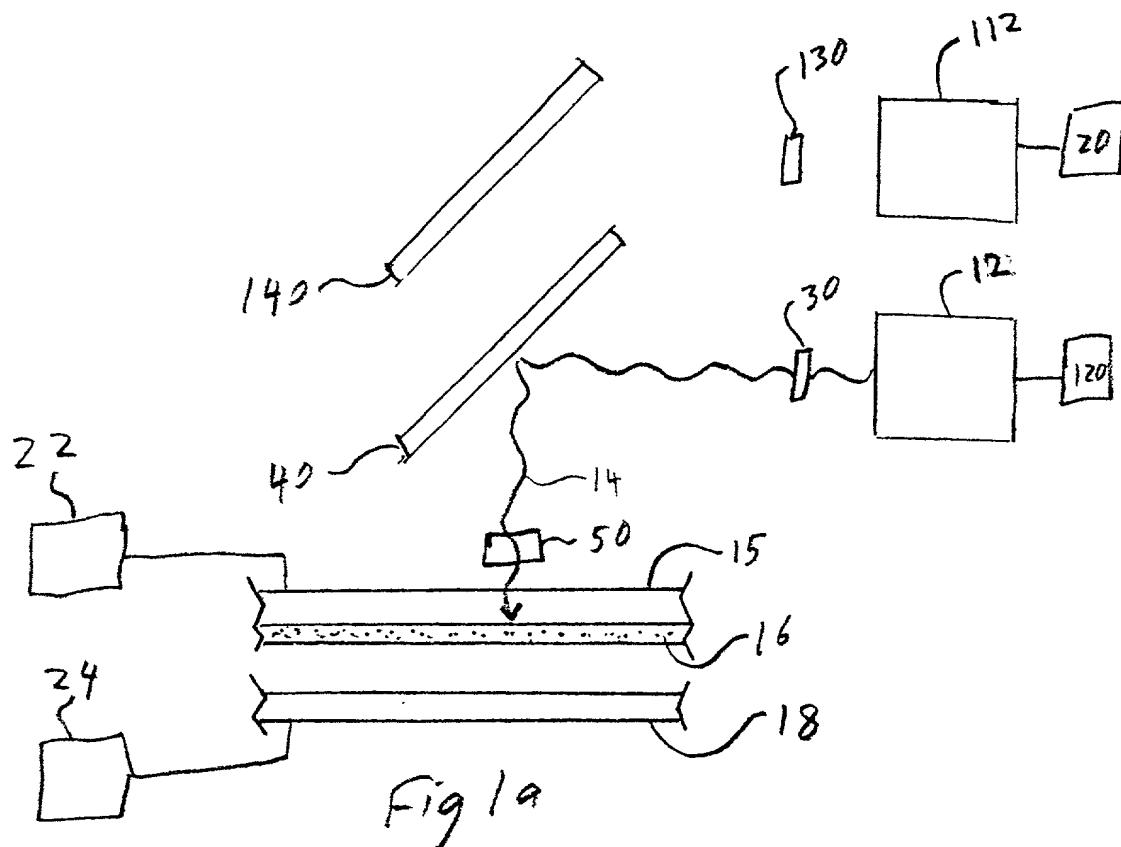
providing a receiving substrate,

directing a pulsed laser beam through the back surface of the target substrate and through the laser-transparent support so that it strikes the coating at a defined target location with sufficient energy to cause the source material to be removed from the surface of the support at the defined location, and so that the source material is deposited at defined receiving location on the receiving substrate, and

directing a laser beam to strike the deposited source material to transform the source material into the material of interest.

## ABSTRACT

A device and method for depositing a material of interest onto a receiving substrate includes a first laser and a second laser, a receiving substrate, and a target substrate. The target substrate comprises a laser transparent support having a back surface and a front surface. The front surface has a coating that comprises the source material, which is a material that can be transformed into the material of interest. The first laser can be positioned in relation to the target substrate so that a laser beam is directed through the back surface of the target substrate and through the laser-transparent support to strike the coating at a defined location with sufficient energy to remove and lift the source material from the surface of the support. The receiving substrate can be positioned in a spaced relation to the target substrate so that the source material is deposited at a defined location on the receiving substrate. The second laser is then positioned to strike the deposited source material to transform the source material into the material of interest.



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Navy Case No. 79,834  
Page 1 of 3

As a below named inventor, I hereby declare that: My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first, and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled: DIRECT-WRITE LASER TRANSFER AND PROCESSING, the specification of which is attached hereto.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign applications for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Number	Country	Filing Date	Priority (Yes/No)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States applications listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

U.S. Prov. Appl. Serial No.	U.S. Filing Date	Status (patented/pending/abandoned)
60/144,662	July 19, 1999	Pending provisional application

**POWER OF ATTORNEY:** As a named inventor, I hereby appoint the following attorneys/and/or agent/s/ to prosecute this application and transact all business in the Patent and Trademark Office connected therewith, and hereby certify that the Government of the United States has the irrevocable right to prosecute this application:

Barry A. Edelberg, Reg. No. 31,012 and Amy Loch Ressing, Reg. No. 45,814

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Naval Research Laboratory  
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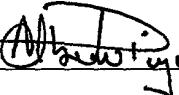
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these

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Page 2 of 3

statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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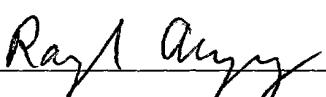
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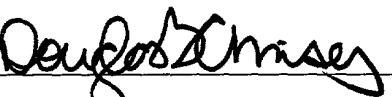
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Page 3 of 3

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**PATENT APPLICATION**  
Docket No.: N.C. 79,834

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Application of: Pique, et al.  
Application No.: To be assigned  
Filed: On even date herewith  
For: DIRECT-WRITE LASER  
TRANSFER AND PROCESSING

Examiner: To be assigned  
Group Art Unit: To be assigned  
July 11, 2000

**NOTICE OF DELAYED FILING OF DECLARATION**

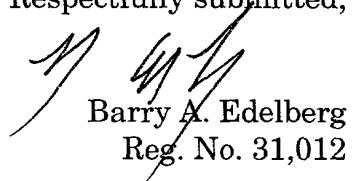
Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

This is to inform the U.S. Patent and Trademark Office that an executed Declaration and Power of Attorney for this application will be submitted at a later date.

Respectfully submitted,

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